

# The Development of High Power Materials with Enhanced Vibrational Velocity and Related Origin Investigation

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## Abstract

Improved piezoelectric materials with higher vibrational velocities are needed to meet the demands of advanced high power electromechanical applications. This paper has reviewed and discussed recent high power materials development, related loss mechanism analysis and possible high power origin investigation. Yb doped  $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Sb,Mn})\text{O}_3$  has been identified as a novel material with a significantly enhanced vibration velocity, as compared to the commercial "hard" piezoelectric. Systematic investigations revealed that internal dipolar fields and applied positive DC biases have the same effect. Both stabilize preferred domain structures, lowering the loss factors. Under high drive conditions, internal dipolar field  $E_{\text{int}}$  should play an important role in increasing mechanical quality factor  $Q_m$ , allowing for the obtainment of higher vibrational velocities within specific thermal stability operational criteria, since heat generation under high field is mainly attributed from extensive dielectric loss, which significantly increases with increasing electric field. Enhanced domain stability by  $E_{\text{int}}$  may be most important in this regard of lowering the loss factors and raising  $Q_m$ . Development of materials with enhanced  $Q_m$  values and high energy densities have been obtained by rare earth modifications of  $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Sb,Mn})\text{O}_3$  ceramics.

## 1. Introduction

Ultrasonic transducers for high power applications, such as ultrasonic motors and piezoelectric actuators have been intensively investigated in recent years<sup>1-5</sup>. The materials with low loss and high vibrational velocity  $v_0$  are desirable for ultrasonic motors application. Higher vibrational velocity results in improved efficiency. Currently, the practical upper-limit of vibrational velocity is restricted by heat generation, as above a certain vibrational level increasing hysteretic effects result in thermal instability. Consequently, approaches to enhance the maximum vibration velocity are an important issue, which to date has proven difficult to achieve.

Heat generation is the most serious problem in ultrasonic motors, which might cause significant temperature rise up to 120°C and therefore serious degradation through depoling of the piezoelectric ceramics. From this consideration the ultrasonic motors require a very hard type of piezoelectric with a high mechanical quality factor  $Q_m$  even at high vibrational velocity. However, it is known that the dissipation of vibrational energy is due to internal friction effects associated with domain dynamics and/or nucleation. Accordingly, heat generation under drive can be represented as a function of vibration velocity, mechanical dissipation factor  $Q_m^{-1}$  and other material parameters, such as mass, length, Young's modules, etc. The dissipated vibrational energy is proportional to the mechanical dissipation factor  $Q_m^{-1}$ , which is related to the area of the ferroelectric hysteresis loop. Previous high-power piezoelectric investigations have shown that  $Q_m$  decreases substantially with increasing vibration level. This results in significant heat generation, limiting the vibrational velocity under high level of drive<sup>6-7</sup>.

In this paper the recent high power materials development, related loss mechanism analysis and possible high power origin investigation will be reviewed and discussed.

## 2. High Power Material Development

### 2.1 Dopant Effects on Ferroelectrics

Small amount of dopants can drastically change the dielectric and electromechanical properties of ceramics. Generally, substituents can be categorized into three classifications<sup>8-10</sup>: lower valent (effective acceptors), higher valent (effective donors), and isovalent. Substituents with lower valence introduce "hard" piezoelectric characteristics, while higher valent substituent induce "soft" ones. "Hard" piezoelectrics have higher  $Q_m$  values, but lower  $k_{31}$  values. On the other hand, "soft" piezoelectrics have lower  $Q_m$  values, but higher  $k_{31}$  values. Dopants will induce either oxygen or lead vacancies in the lattice, forming mobile or

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immobile quenched charged defects, such as dipoles and local stress fields<sup>11-12</sup>. Figure1 illustrates the crystal deficiencies in a perovskite structure caused by acceptor or donor elements<sup>5</sup>. Acceptor ions cause the formation of dipole moment, which is composed of an acceptor defect and an oxygen vacancy. The deficiencies are generated at high temperature during sintering, however the oxygen vacancies are still movable below the Curie temperature, even at room temperature, since the oxygen ion and vacancy are close to each other, the distance between each other is only about 2.8 Å. In contrast, for donor modified PZT, the lead ion and A-site vacancy are separated by the oxygen atom, therefore the transport would not happen at low temperature.

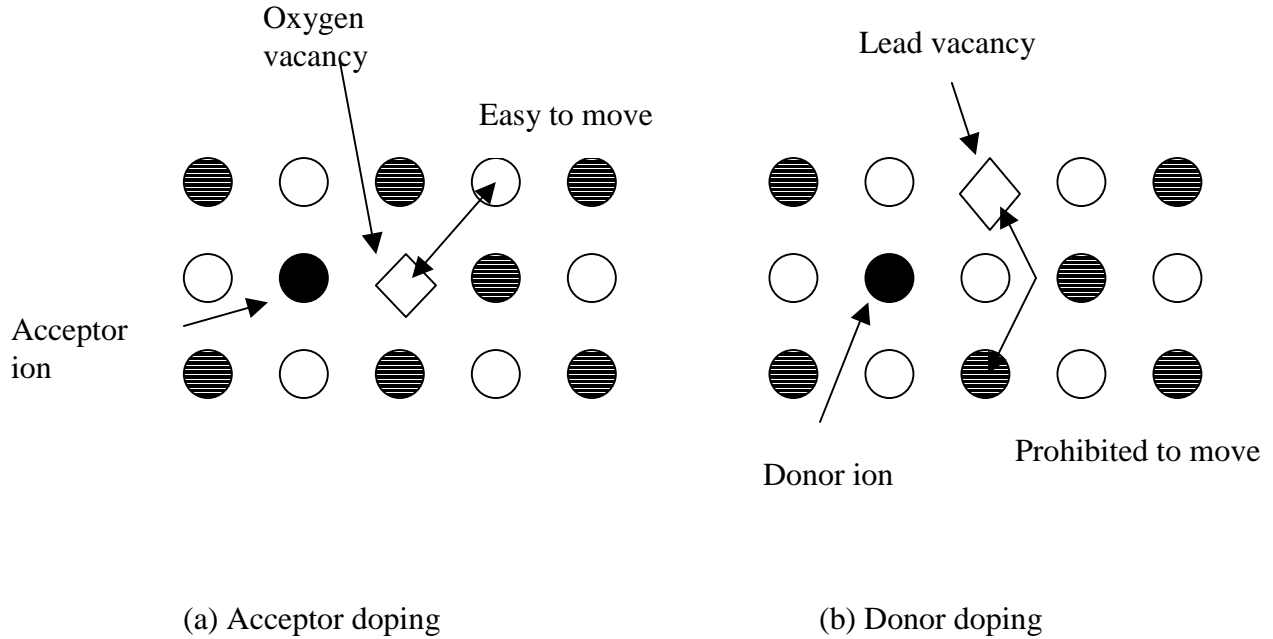


Figure 1 Crystal deficiencies in PZT for acceptor (a) and donor (b) dopants<sup>5, 8, 9</sup>

Hagimura and Uchino studied the doping effects on field induced strain in  $(\text{Pb}_{0.73}\text{Ba}_{0.27})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$  ("soft" PZT). Figure 2 gives the definition of the maximum strain and the degree of hysteresis<sup>13</sup>. Figure 3 shows the different types of dopant substitution effects on the strain and hysteresis degree<sup>13</sup>. It can be seen that for off resonance driving condition typical donor (such as  $\text{Nb}^{5+}$ ) modified PZT shows high strain and relatively low hysteresis while the typical acceptor (such as  $\text{Fe}^{3+}$ ) doped one shows low strain. Rare earth elements modified ceramics shows an intermediate strain and hysteresis level, as compared to the above 2 groups. Table 1. summarizes the characteristics and application areas of the "soft" and "hard" types of piezoelectrics<sup>14</sup>.

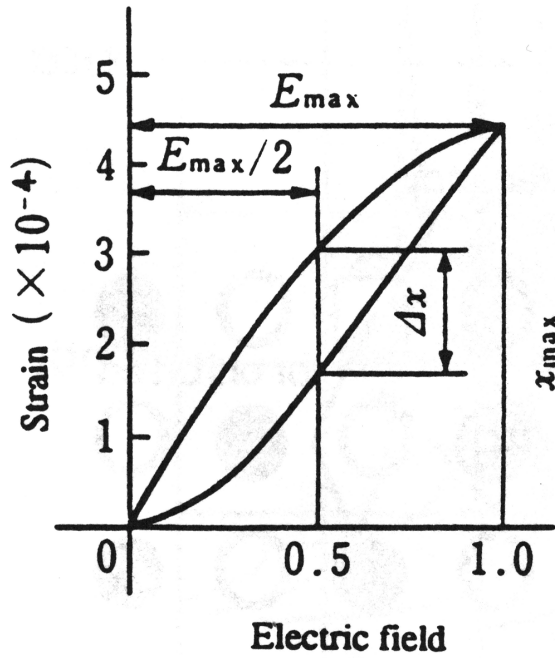


Figure 2 Definition of the maximum strain and the degree of hysteresis <sup>14</sup>

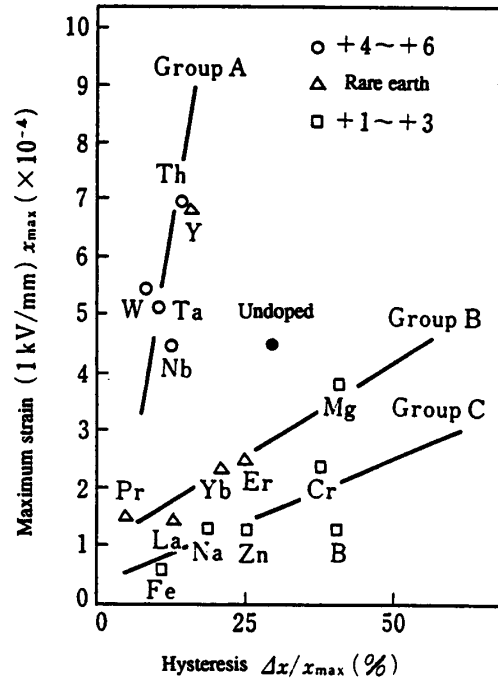


Figure 3 Dopant effect on the maximum strain and hysteresis degree in  $\text{Pb}_{0.73}\text{Ba}_{0.27}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$  based ceramics <sup>14</sup>

Table 1 <sup>14</sup>

	d	k	$Q_m$	Off Resonance Application	Resonance Application
Soft Piezo (PZT-5H)	High	High	Low	High Displacement ( $L = dEL$ )	Heat generation (demerit)
Hard Piezo (PZT-8)	Low	Low	High	Low strain (demerit)	High AC Displacement ( $L \propto Q_m \cdot dEL$ )

Long Wu (1982) <sup>10</sup> systematically investigated the rare earth elements doping effects on pure PZT ceramics. It was proposed that the trivalent ion distribution among A- and B-sites determined the properties of lead containing piezoelectric ceramics. According to Goldschmidt rules, the radii difference between substituent ion and the original A- or B- sites ions should be less than 15% <sup>9</sup>. Based upon tolerance factor considerations, in addition to gravimetric and lattice parameter variations, it was determined that in PZT ceramics, RE substituents are equally probable to occupy A-site and B-site positions for species with an ionic radii between 0.96 Å and 0.97 Å. When rare earth ions substituted A-site, the excess charge must be compensated by lead vacancy in perovskite structure; when dopant ions enter into (Ti, Zr) sites, the oxygen vacancies are generated for the charge compensation <sup>15</sup>. For all of the rare earth elements investigated in this study (from La to Lu) the ionic size is smaller than  $\text{Pb}^{2+}$  but larger than  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$ , so depending on the substituent ion size, both A- and B- sites substitution are possible. Hagimura et al. <sup>16</sup> have reported that in PZT ceramics RE elements bigger than Gd induce “soft” characteristics, which include decreased coercive field ( $E_c$ ), decreased mechanical quality factor  $Q_m$ , increased piezoelectric constants and electromechanical coupling coefficients. Whereas, substitution with smaller RE species have opposite trends, introducing “hard” characteristics. Figure 4 gives the rare earth doping effects on  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ . It can be seen that with increasing rare earth substituent radius, the electromechanical coupling factor and dielectric constant increase, but the mechanical quality factor  $Q_m$  decreases <sup>10</sup>.

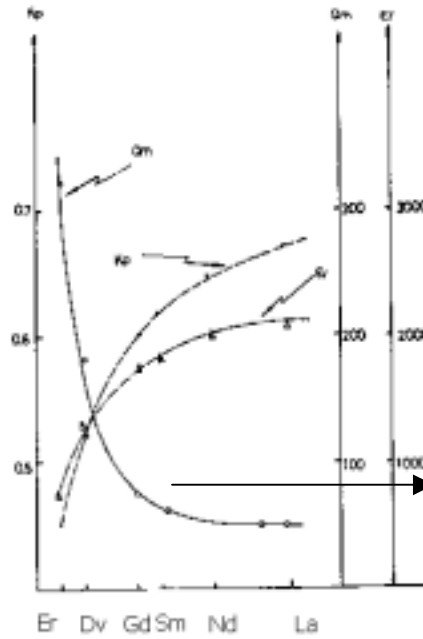


Figure 4 Rare earth doping effects on the electromechanical coupling coefficient  $k_p$ , dielectric constant  $\epsilon_r$  and mechanical quality factor  $Q_m$  of  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  based ceramics<sup>10</sup>

## 2.2 Ferroelectric under High Level Driving Condition

Several effects are known to happen under high vibration level. These include: (i) a shift of the resonance frequency  $f_r$ ;<sup>17-19</sup> (ii) an appearance of a jump and/or a hysteresis in the admittance spectrum during a frequency sweep<sup>20-22</sup>; (iii) a decrease of  $Q_m$ <sup>23</sup>; and (iv) heat generation (due to the lower  $Q_m$ ) that not only degrades the electromechanical properties<sup>24</sup>, but may also result in thermal instability problems.

It is also noteworthy that the mechanical vibration amplitude at the resonance frequency is proportional to  $Q_m$  value. However, the data obtained by a conventional impedance analyzer driving at low field (1V) does not provide the high power performance due to the elastic nonlinearity under high drive. Mechanical quality factor  $Q_m$  significantly decreases when the vibration beyond a certain level, which causes significant heat generation<sup>23</sup>. Figure 5 shows the mechanical quality factor  $Q_m$  as a function of Zr mole fraction in Fe modified PZT at 2 different driving levels. At low drive (vibration velocity 0.05m/s) the lowest  $Q_m$  value was found at rhombohedral-tetragonal morphotropic phase boundary (52/48), but the same composition at high level of drive (vibration velocity 0.5 m/s) was associated with highest  $Q_m$  value among all of the investigated compositions<sup>25</sup>. A possible explanation for this is that at resonance heat generation is mainly attributed from intensive mechanical loss, which consists of extensive dielectric and mechanical loss. Under low field drive, mechanical loss which is associated with non-180° domain is the main reason for heat generation; however, with increasing the applied electric field extensive dielectric loss which is associated with 180° domain will significantly increase, and became the main contribution for heat generation, as increasing of electric field level has only gradual influence on the extensive mechanical loss<sup>26</sup>. Figure 6 gives how the mechanical quality factor  $Q_m$  changes with increasing vibrational velocity at resonance or antiresonance drive as well as corresponding temperature rise for these 2 types of drive. It is noteworthy that above a certain level of drive the  $Q_m$  value significantly dropped which results in drastic temperature rise. The possible vibrational velocity is limited by the heat generation since any additional

input energy will be converted into heat rather than power output. It is difficult to reach a high vibration velocity  $v_0$  and a low heat generation ( $T$ ), as  $T$  is known to be proportional to  $v_0^2$ <sup>27</sup>. From a practical perspective, the maximum vibrational velocity can be defined as the  $v_0$  which produces a  $T = 20^\circ\text{C}$ . For the commercialized “hard” type PZT  $v_0$  ( $T = 20^\circ\text{C}$ ) is about 0.3~0.4 m/s. To obtain better performance, the antiresonance drive mode was proposed<sup>26, 28-30</sup>.

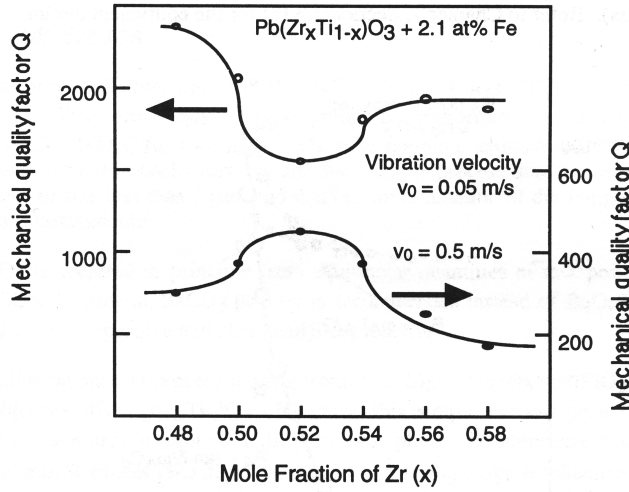


Figure 5 Mechanical quality factor  $Q_m$  as a function of basic composition  $x$  in  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  doped with 2.1 at.% Fe ceramics, driven at 2 different vibration velocities (0.05 and 0.5 m/s)<sup>25</sup>

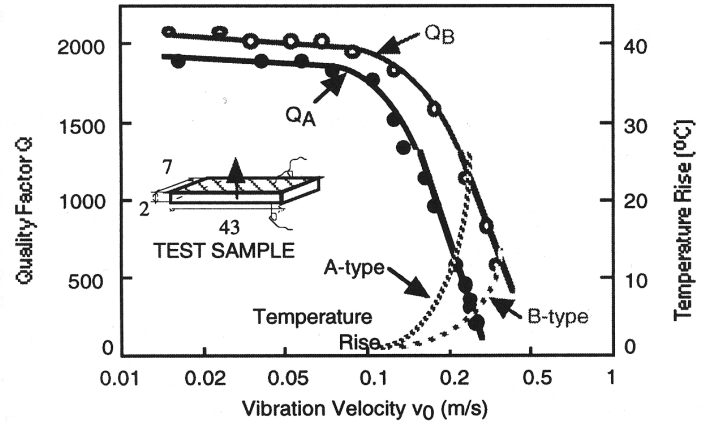


Figure 6 Mechanical quality factor  $Q_m$  and temperature rise as a function of vibration velocity from a longitudinal vibrator PZT driven at resonance (A) and antiresonance (B) modes, respectively<sup>26, 28-30</sup>

The common approach for improving properties of PZT ceramics is to introduce dopants or substituents. Two general types of aliovalent substituents in ferroelectrics have been identified<sup>11, 31</sup>. These are substituents electrically compensated by defects of the random-field type and of the mobile type. The differences between lower and higher valent substitutions might be partially explained in the terms of defect mobility near or below the phase transformation temperature<sup>11, 31</sup>. Internal dipolar field will stabilize domain configuration, which brings “hard” characteristics to ceramics. “Soft” characteristics are from polarization irregularities introduced by defects of the immobile random-field type<sup>32-33</sup>.

Figure 7 gives the temperature rise as a function of vibration velocity for PZT modified with different type of dopants. By introducing Fe into PZT ceramics the vibration velocity has been increased, but Nb substitution caused decreased vibrational velocity as compared to the undoped  $\text{Pb}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$  ceramics<sup>28</sup>.

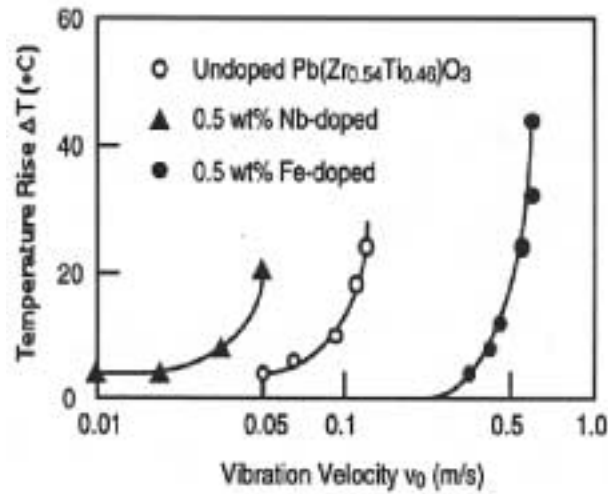


Figure 7 Temperature rise as a function of vibration velocity for PZT modified with different type of dopants <sup>28</sup>

### 2.3 $Pb(Zr,Ti)O_3$ - $Pb(Sb,Mn)O_3$ Based High Power Material Development

The vibrational velocity  $v_0$  is proportional to the product of the mechanical quality factor  $Q_m$  and the electromechanical coupling factor  $k$ , for example,  $v_0 \propto Q_m k_{31}$  for a rectangular plate working under  $d_{31}$  mode <sup>19,25,32</sup>. Consequently, for high-power applications, a piezoelectric material is needed which has simultaneously both high  $Q_m$  and  $k_{31}$  values. Practically, the development of a material with significantly higher values of  $v_0$  has been in vain, as previous investigations have shown that either  $Q_m$  or  $k_{31}$  can be enhanced only at the expense of the other.

Interestingly,  $Cr^{+3}$  and  $U^{+3}$  substituents have previously been reported to induce some attributes of “hard” and “soft” piezoelectric characteristics <sup>10,34</sup>. However, further investigations have not been reported. Investigations of rare-earth (RE) substituents on piezoelectric properties have in general not been reported. Although, Hagimura et al. <sup>16</sup> have reported RE doping effects in PZT ceramics. However, before our study no reports have been published concerning the effects of rare earth species on the piezoelectric vibration velocity.

Pseudo-ternary crystalline solutions of  $Pb(Zr,Ti)O_3$ - $Pb(Sb,Mn)O_3$  (PZT-PSM) have been reported to have high mechanical quality factor  $Q_m$ , high electromechanical coupling factor and high thermal stability when driving under high level of vibration as well as significantly high vibration velocity, as compared to other PZT based ceramics. In this system, a maximum vibration velocity (defined by an rms value which raises the temperature to 20°C above room temperature) of 0.6 m/s has been found <sup>27</sup>.  $Pb(Sb_{2/3}Mn_{1/3})O_3$  does not exist as a single phase <sup>35</sup>. However, PZT with small ratio of PSM can form single phase of perovskite structure.

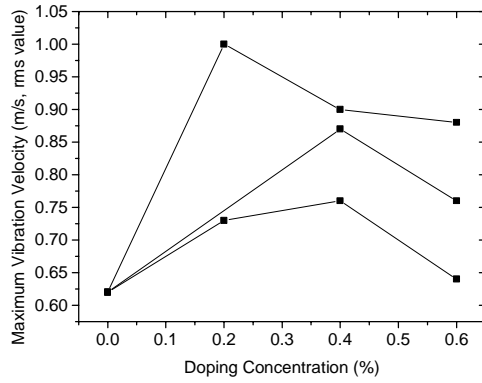


Figure 8 The maximum vibration velocity of PZT-PSM Yb, PZT-PSM-Eu and PZT-PSM-Ce vs. doping concentration.

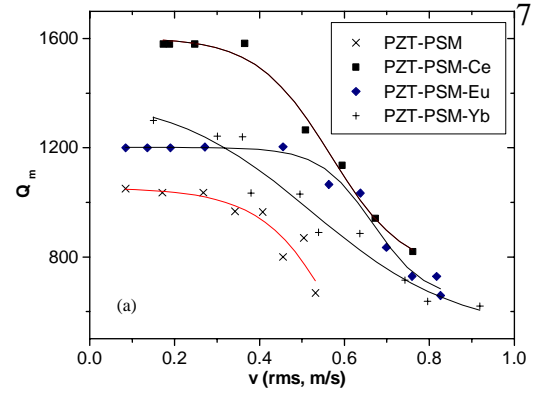


Figure 9 Mechanical Quality Factor  $Q_m$  as a function of  $v_{rms}$  for PZT-PSM and PZT-PSM modified with 0.2 at.% Ce, Eu or Yb

Most RE transition-metal (from Yb to Ce) substituents investigated in our 4-year study have been shown to result in combinative "hardening" and "softening" effects in PZT-PSM ceramics, which is different from that of RE doping in PZT ceramics. In addition, under high level drive conditions,  $v_o$  has been significantly increased by all of RE substitution investigated, relative to that of the base PZT-PSM ceramic. PZT-PSM modified with 0.2 at.% Yb has been identified as a new high-power material. It has a  $v_o$  ( $T=20^\circ\text{C}$ ) as high as 0.9 m/s (rms value) under an electric field of 10 kV/m (rms value), which is about 1.6 times higher than that of conventional PZT ceramics where  $v_o$  ( $T=20^\circ\text{C}$ ) is equal to 0.4 m/s. Figure 8 summarizes the results of  $v_o$  ( $T=20^\circ\text{C}$ ) for all Yb, Eu or Ce modified PZT-PSM as a function of doping concentration  $x$ . From this figure, significant enhancements in  $v_o$  ( $T=20^\circ\text{C}$ ) can be seen upon substitution with either element. With 0.2 at.% Yb doping, the rms vibration velocity has been increased from 0.60 m/s ( $x=0$  at.%) to 0.9 m/s. It is also clear that Yb produces the highest values and at significantly lower concentrations. At higher concentrations,  $v_o$  ( $T=20^\circ\text{C}$ ) decreased for all of Yb, Eu and Ce substituted materials<sup>36</sup>.

Mechanical quality factor  $Q_m$  has been significantly increased upon several of RE substitution under both high and low level of drive. Figure 9 shows  $Q_m$  as a function of  $v_{rms}$  for PZT-PSM and PZT-PSM modified with 0.2 at.% Ce, Eu or Yb. From this figure, it can be seen that small concentrations of Ce, Eu or Yb enhanced  $Q_m$  very significantly, under both low and high level driving conditions. The thermal stability is significantly increased due to the improvements in  $Q_m$  introduced by RE substitution. The existence of a threshold vibration velocity for the onset of nonlinearity in  $Q_m$  can also be seen in this figure. The results of this section clearly demonstrate the effectiveness of RE substituents in improving the high-power characteristics of ultrasonic resonators. RE substituents significantly improve  $Q_m$ , under both low and high power drive conditions. However, in all cases, significant decreases in  $Q_m$  eventually occur with increasing drive field. This decrease in  $Q_m$  is due to hysteretic polarization effects, which result in energy dissipation

### 3. Domain Motion and Loss Mechanism in Piezoelectrics

Domain motion and loss mechanism are very important issues for heat generation investigation. The traditional continuum approach does not fit the domain kinetics under small or large signal excitation perfectly. It has been found that only 25-30% of the piezoelectric response under weak field excitations in poled soft ferroelectrics can be accounted for by Landau-Devonshire phenomenology<sup>38</sup>. It has been proposed that the remaining 75% of the electromechanical response and a significant fraction of the dielectric response are due to domain boundary contributions.

Domains contribute significantly to the electromechanical and mechanical non-linearities, although the mechanism of this contribution remains in question. In addition, domain contributions significantly impact the imaginary components of the responses<sup>39, 40</sup>. Haerdtl<sup>40</sup> has written a review article on electrical and mechanical losses in ferroelectric ceramics. Four types of contribution to losses were proposed and these are: (1) domain wall motion, (2) a fundamental lattice contribution, which should also

happen in domain free monocrystals, (3) a microstructural contribution, which occurs typically in polycrystalline samples, and (4) a conductivity contribution in highly-ohmic samples. However, in typical piezoelectric ceramics, the loss due to domain wall motion was believed to significantly exceed the other three types.

It was found that besides dielectric and mechanical loss, piezoelectric loss is large enough not to be ignored<sup>26, 42</sup>. Loss or hysteresis is a very important issue in piezoelectric applications. It is noteworthy that the extensive dielectric loss increases significantly with the increasing of the applied electric field, while the extensive elastic loss is rather insensitive to the applied compressive stress. For off resonance driving at high level excitation heat generation is caused mainly by the intensive dielectric loss, while for resonance drive intensive mechanical loss is the main contribution to heat generation. Considering that both intensive dielectric and mechanical losses are composed of extensive dielectric and mechanical loss and that the extensive dielectric loss changes significantly with the external field, it seems under high level of excitation for both resonance and antiresonance modes heat generation mainly comes from the extensive dielectric loss<sup>26</sup>.

Uchida and Ikeda treated the domain reorientation in ceramics statistically, assuming that grains (small crystallites) are crystallographically randomly oriented<sup>43, 44</sup>. 180° domain reversal is the main contribution to polarization while 90° domain rotation contributes to strain. It was proposed that by applying an external electric field 180° domain reversal occurs rapidly whereas 90° domain rotates slowly<sup>45</sup>.

For high power ultrasonic applications a large vibrational level is necessary in order to gain high power output, however significant heat generation degrades the vibrational performance drastically since the vibration strain at resonance mode is proportional to the mechanical quality factor  $Q_m$  (the inverse value of mechanical loss). Above a certain vibration level  $Q_m$  decreases significantly with driving amplitude (see 2.2). Therefore for an ultrasonic application a very “hard” piezoelectric with high mechanical quality factor  $Q_m$  even at high level driving is desirable for heat suppression<sup>5, 14</sup>.

Previous investigations have shown that domain wall motion/vibration may contribute significantly on the magnitude of loss factors<sup>39, 40</sup>. The observed large-signal losses were attributed to the destabilization of domains. Pinning or clamping of the domain motion results in reduced mechanical and dielectric losses. By introducing acceptor type of dopants, “hard” piezoelectrics exhibit near linear behavior of polarization under AC cycling of the field, which results in greatly reduced hysteretic losses and hence significantly reduced heat generation.

### 3. High Power Piezoelectric Characteristic Origin Investigation

#### 3.1 Internal Bias Field

A shift of ferroelectric hysteresis curve along the E-axis without any external DC bias is called an internal bias field, which was first observed in natural colemanite crystals<sup>46, 47</sup>. Triglycine sulfate (TGS) has been intensively investigated which shows internal bias field by doping with L-alanine dipoles or by introducing other types of defects causing dipolar behavior<sup>48-51</sup>. Arlt investigated the internal bias field development in Ni doped BaTiO<sub>3</sub>. Figure 10 shows the P-E hysteresis and transient

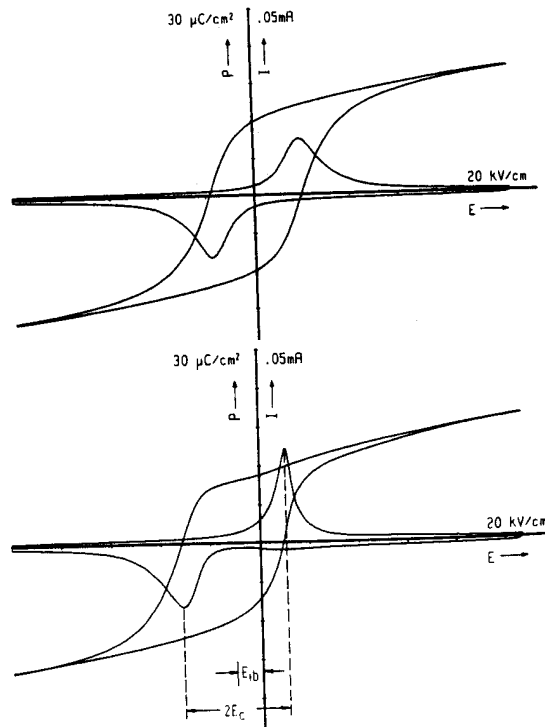


Figure 10 Typical hysteresis loop and transient current loop for “freshly” poled (a) and aged (b) Ni-doped BaTiO<sub>3</sub>. (b) gives the experimental definition of internal bias field  $E_{ib}$ <sup>52</sup>

current loops for “freshly” poled (less than 15 min after poling) and aged specimen (more than one month after poling), respectively, which provides the common definition of experimentally observed internal bias field<sup>52</sup>. Also, it was found that the coercive field of LiTaO<sub>3</sub>, both in forward and reverse directions, increase with time after the domain is switched. The coercive field drops when the domain is inverted, then gradually recovers. This process was found to be associated with light intensity<sup>53</sup>.

Lower valent substitution results in enhanced transport characteristics at moderately elevated temperatures, even at room temperature, as the oxygen atoms are interconnected residing on octahedral sites and are relatively large. The “hard” piezoelectric characteristics were proposed to be due to polarization pinning by mobile defect complexes. On other hand, in higher valent substituted PZTs (such as Nb<sup>5+</sup>, Sb<sup>5+</sup>, W<sup>6+</sup>), charge compensation is generally achieved by Pb vacancies. Pb atoms are not interconnected occupying the faces of the perovskite cube; thus, they do not result in enhanced transport and contribute to the domain wall pinning. Moreover, the donor doping compensates the original p-type characteristics of PZT due to the Pb evaporation during sintering. The “soft” piezoelectric characteristics have been attributed to near-randomly distributed point defects.

On the other hand, in lower valent modified ferroelectrics, a shift of P-E curves along field axis was observed, without application of DC electric field (E). The shift of the P-E curve is due to an internal dipolar field, which prevents (or stabilizes) the material from depoling under moderate E. The internal dipolar field  $E_{int}$  can be identified from an asymmetry in the P-E response. A relaxation model has been used to semi-quantitatively calculate the time dependence of the internal dipolar field<sup>52</sup>.

After poling, a relatively fast first stage of aging is known in both “hard” and “soft” PZTs, which has been attributed to the release of grain boundary stresses and of charge accumulation. In addition, for “hard” PZTs, a secondary relatively slow stage of aging is known at longer times<sup>54</sup>. Few investigations have studied the related property changes, due to the stabilization of the internal dipolar field with time. Only the time dependence of the internal dipolar field and dielectric constant within several hours after poling in Ni doped BaTiO<sub>3</sub><sup>55,56</sup> has been studied. An increase in the internal dipolar field and a decrease in the dielectric constant were reported. Before our study, no systematic study has been performed on the time dependent piezoelectric, elastic and loss characteristics of ferroelectrics, within 48 hours after poling, while this is a very important issue for understanding the “hardening effect” in piezoelectrics. During this short

time period after poling, polarization pinning or clamping may become increasingly complete, resulting in enhanced “hardening”.

### 3.2 Time Dependence of Mechanical Quality Factor $Q_m$

During our experimental, immediately after poling, specimens were short-circuited by connecting the top and bottom electrodes. To exclude an initial and faster aging mechanism that has previously been reported, all measurements were begun precisely 10 minutes after poling<sup>54</sup>. This allowed enough time to exclude initial or anomalous aging, and to concentrate on the secondary mechanism related to the build-up of an internal dipolar field. This care was taken in order to place all specimens in as similar as possible defect configurations, as previous investigations have shown a time-temperature-field interdependent history on the defect complex distributions in “hard” PZTs<sup>11,31</sup>. Figure 11 shows  $Q_m$  as a function of time for commercial “hard” and “soft” PZTs, which had been annealed and then “freshly” poled. In addition, results are shown in this figure for PZT-PSM-Yb and PZT-PSM. Commercial “hard” PZTs exhibited a significant increase in  $Q_m$  with time, similar to that shown for PZT-Mn. The value of  $Q_m$  increased from ~400 to ~1000, for  $10 < t < 2800$  minutes. The long time values of  $Q_m$  for PZT-PSM and PZT-PSM-Yb were even higher, approaching 1600 at  $t=2800$  minutes. However, for “soft” PZTs, the value of  $Q_m$  was essentially time independent. These results clearly demonstrate an important difference in the time dependence of  $Q_m$  between “hard” and “soft” PZTs. However, it must be kept in mind that these investigations have been performed at predefined time-temperature-field histories, and may yield different slopes and degrees of hardness at a set time after poling depending upon the defect distribution.

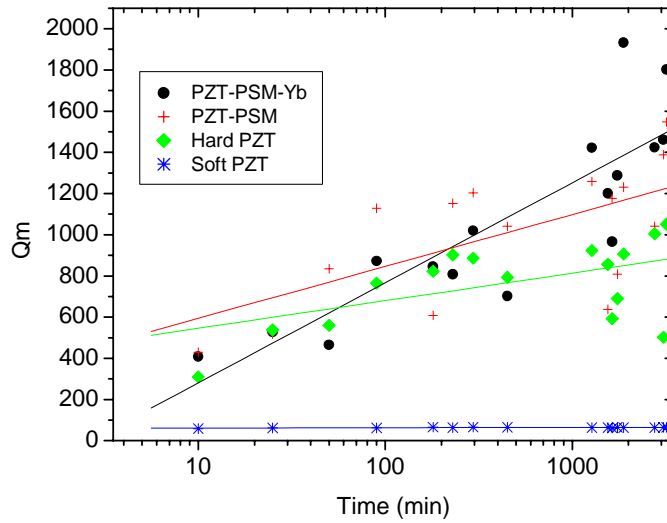


Figure 11  $Q_m$  as a function of time for multiply substituted PZTs.

In an aged condition, “hard” PZTs have P-E curves that are shifted on the E axis. To switch polarization, E must exceed the sum of the coercive field  $E_c$  and  $E_i$ <sup>57</sup>. Figure 12 shows the P-E hysteretic response for PZT-PSM-Yb. After  $t=10$  minutes, the P-E loop was symmetric, similar to the commercial “hard” PZT. After 48 hours aging, an obvious shift towards the negative E direction was observed. After one month aging,  $E_i$  was  $\sim 9$  kV/cm, which is higher than that of commercialized “hard” PZT ( $\sim 5$  kV/m) and “soft” PZT (0 kV/cm) ceramics. Accordingly, the remnant polarization and hysteretic losses were significantly reduced by aging, relative to the “freshly” poled ( $t=10$  minutes) specimen.

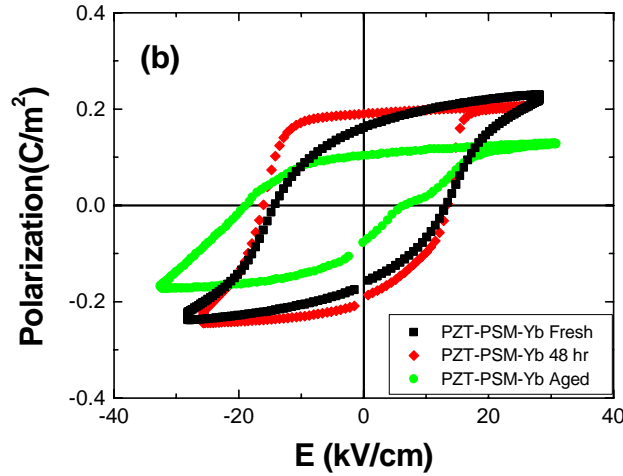


Figure 12 P-E hysteretic response for various PZTs taken at times of 10 min, 48 hrs and 1 month after poling for PZT-PSM-Yb

### 3.4 Vibration Behavior Measurement

The mechanical vibration amplitude at resonance is  $(8/\pi)Q_m$  times that of the off-resonance displacement, which is  $d_{31}EL$  (where  $L$  is specimen length) for a longitudinal vibration plate. Thus, the value of  $Q_m$  has a significant influence on piezoelectric materials driven at resonance under high-power conditions<sup>28-30</sup>. Under high drive conditions,  $E_{int}$  should play an important role in increasing  $Q_m$  therefore increasing the vibrational velocity within a specific temperature range. Dielectric loss is believed to be mainly associated with  $180^\circ$  domains; whereas mechanical loss is due to non- $180^\circ$  domains<sup>26</sup>. Enhanced domain stability by  $E_{int}$  may be most important in this regard of lowering the loss factors and raising  $Q_m$ . Materials with high  $E_{int}$  (i.e., reduced loss and higher  $Q_m$ ) but reduced pinning effects would be ideal. Rare earth modified PZTs have excellent combinatorial properties in these regards.

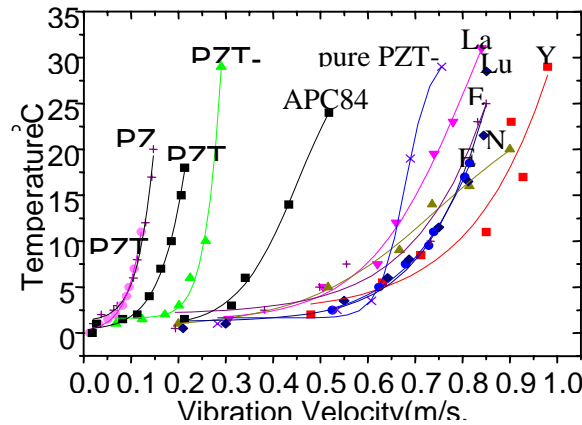


Figure 13 Temperature rise as a function of the vibrational velocity  $v_o$  (rms value) for various “soft” and “hard” PZTs.

Inspection of figure 13 will demonstrate that rare-earth modified PZT-PSM materials all have exceptionally high vibration velocities within the temperature stability range of operation. The vibration velocity was found to be maximum for PZT-PSM-Yb, with a value of  $v_o=0.9$  m/sec. This value is much higher than those of commercial “hard” PZTs (APC841), which had vibration velocities less than 50% of this value within the accepted thermal tolerance range; and than those of Mn-modified “hard” PZTs, which had values less than 66% of the value.

Normally, as a material is made harder, its induced polarization and strain changes are also made smaller. However, in the case of RE modified PZT-PSM, this was not the case. A unique combination of enhanced polarization and higher  $Q_m$  values was obtained. This is illustrated in figure 14, which shows the P-E response for a rare earth modified PZT-PSM and a Mn-modified PZT. In this figure, the induced polarization changes for the rare earth modified PZT-PSM can be seen to be greater than 2x that of the Mn-modified PZT. Rare earth modified material has significantly higher  $P_r$ , while at the same time having significantly higher mechanical quality factors. Considering rare earth modified PZT-PSM has the highest  $E_{int}$  among all of the investigated specimens, clearly, internal electric fields are essential for high-power applications of piezoelectric materials.

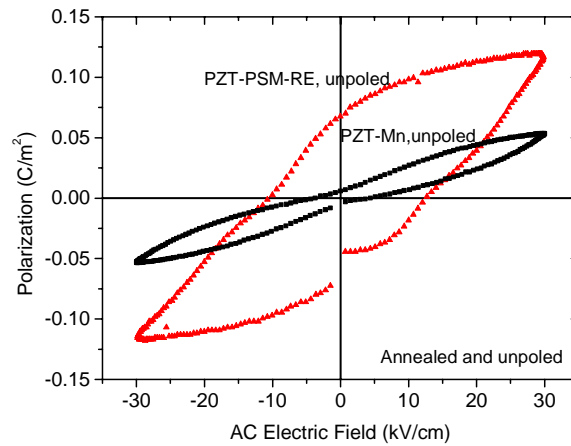


Figure 14 P-E hysteresis for annealed and unpoled “hard” piezoelectrics (a) PZT-Mn (b) RE modified PZT-PSM

### 3.5 Possible Model

Although in the initial stage the domain wall pinning effect caused by local interaction of dipole defect clusters with domain boundaries might be the dominating factor for domain stabilization, in lower valent substituted PZTs, the relatively slow development of an internal dipolar field seems to be the main contribution to “hard” piezoelectric behavior. Figure 15 illustrates development of  $E_i$  with time. Usually a couple of acceptor ion and oxygen vacancy makes a defect dipole moment. The defect dipole should be oriented during poling process. The substituent/oxygen vacancy dipolar pairs can change their orientation after removing the poling electric field, via oxygen vacancy diffusion amongst neighboring equivalent sites within the oxygen octahedra. In the illustration, by applying of large amplitude DC poling electric field, the B-site ion moved upward already. After shutting off the poling field, the oxygen vacancy became unstable and because of the ferroelectric displacements, the upper oxygen has more room to diffuse into the oxygen vacancy, than the lower lying one. Thus, there is an energetically favored site for diffusion, as predicted by Arlt in  $BaTiO_3$ <sup>52</sup>. Based on this assumption, the localized defect dipole moment is thermally enhanced with time, leading to the generation of the internal dipolar field with the same direction as the spontaneous polarization, as the internal dipolar field is provided by the Lorentz factor multiplied by the localized polarization. Also, Arlt proposed that oxygen/oxygen vacancy site exchange will occur dominantly within  $10^5$  seconds, in agreement with our experimental result that  $Q_m$  increased for  $0 < t < 2800$  minutes.

Oxygen diffusion is a thermally activated process. Therefore, at elevated temperatures, aging and the development of  $E_i$  will occur faster. The activation energy for diffusion of oxygen vacancy is about 1.1 eV for BaTiO<sub>3</sub>, and about 1.2 eV for PZT. Thus, the dipolar orientation needs considerable time to establish thermodynamic equilibrium<sup>55</sup>. Therefore, in a poled specimen, the increase of  $Q_m$  with time is not a fast process. Once it develops, the internal dipolar field and spontaneous polarization ( $P_s$ ) stabilize each other.

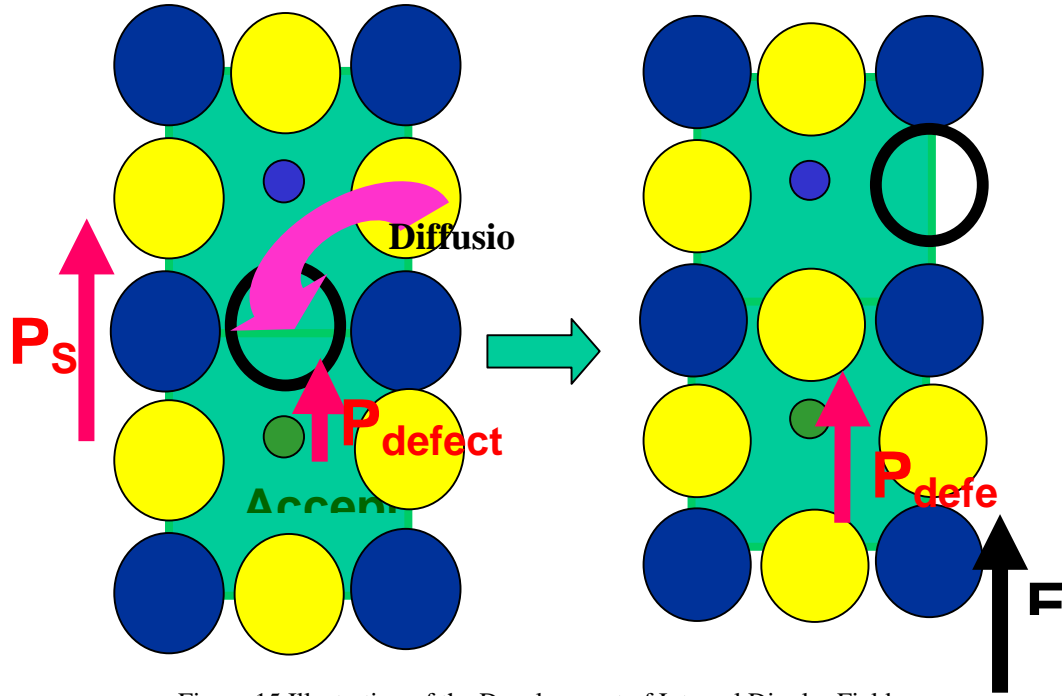


Figure 15 Illustration of the Development of Internal Dipolar Field

An internal dipolar field has been reported to have little influence on the intrinsic (single domain, single crystal) ferroelectric properties<sup>46</sup>. In this case, clearly, the reduction of domain wall contributions by an internal dipolar field is the main reason for increase of  $Q_m$  with time and for the aging in  $k_{31}$ ,  $K$  and  $S_{11}^E$ , several hours after poling. The enhancement of the internal dipolar field in PZT-PSM-Yb, in comparison with PZT-PSM can be explained by an additionally generated oxygen vacancy by rare earth doping (Yb), which increases or stabilizes the localized dipole moment.

#### Experimental Verification

If the above argument that  $E_i$  developed after/during poling through oxygen diffusion is the main contribution to domain stabilization in poled specimens is true, then “hard” characteristics (i.e., the increase of  $Q_m$ , and decrease of  $K$ ,  $k_{31}$  and  $S_{11}^E$ ) should be significantly altered by removal of the internal dipolar field. Afterwards,  $Q_m$  should recover with time, as  $E_i$  redevelops. Our experimental result confirmed this hypothesis.

Previously aged specimens were subjected to a re-poling along the same direction. Figure 16 shows  $Q_m$  as a function of time after this secondary re-poling. The poling condition was maintained the same as the first poling. For PZT-PSM-Yb,  $Q_m$  dropped on re-poling to  $\sim 800$ , it then subsequently increased again with time, finally reaching its value prior to repoling of  $Q_m=1700$ . Similar results were obtained for PZT-PSM and PZT-Mn after a secondary poling. This result confirmed the conjecture that internal dipolar field is the main contribution to domain stabilization in aged “hard” specimens.

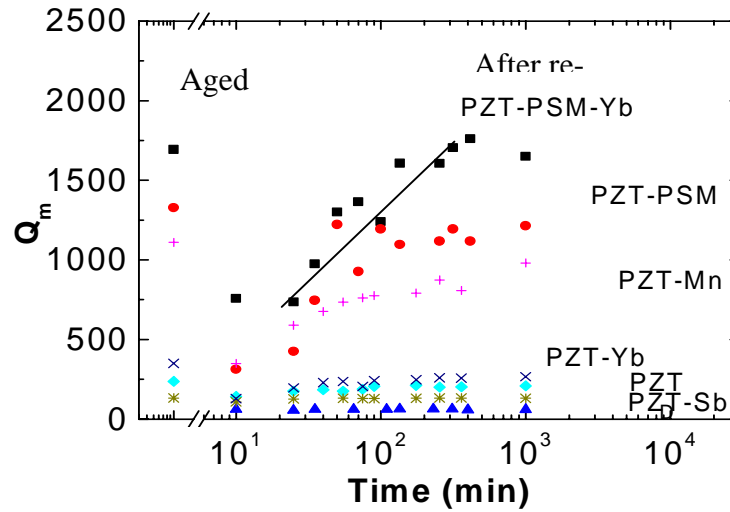


Figure 16 Time dependence of  $Q_m$  after a secondary repoling from a previously aged condition.

### 3.6 The Comparison of External DC bias and Internal Dipolar Field

The free energy modified by internal dipolar field is in a similar way as external DC electric field<sup>46</sup>. In transducer applications, sometimes an externally positive DC bias is required to stabilize domain configuration and prevent depoling. When positive DC bias is applied, a decrease in  $K$ ,  $k_{31}$  as well as  $S_{11}^E$  has been observed<sup>54</sup>. The P-E hysteresis apparently shifts along an electric field axis also. For a well poled piezoelectric ceramic, an additional positive DC bias does not contribute much for increasing the total polarization, rather it stabilizes the domain configuration and suppresses domain wall motion<sup>58</sup>. However, systematic investigations of the influence of applied DC bias have not been performed on “freshly” poled “hard” PZTs, where the internal dipolar fields should be small.

Figure 17 shows the value of  $Q_m$  as a function of applied DC bias ( $E_{dc}$ ) for a “freshly” poled rare-earth modified PZT-PSM specimen. Ten minutes after poling, the value of  $Q_m$  was only 362; however, with increasing positive  $E_{dc}$ , a significant increase of  $Q_m$  was observed. For  $E_{dc}=1.5$  kV/cm,  $Q_m$  was dramatically increased to over 1300. Further increase of  $E_{dc}$  did not result in additional noticeable increments in  $Q_m$ . Figure 18 shows the effect of  $E_{dc}$  on a “freshly” poled commercial “soft” PZT. The value of  $Q_m$  was found to be increased by  $E_{dc}$ . “Soft” PZTs are known not to have an  $E_{int}$ , but rather are believed to have defects of the random-field type. The combination of results in figure 7.1 indicates that internal dipolar fields stabilize domains, in a similar manner as applied positive DC biases. Both types of fields seemingly act linearly combinatorially, as conjugates to the polarization.

Applied DC biases shift the P-E and  $\epsilon$ -E responses along the E axis for both “hard” and “soft” materials; however, built-in dipolar fields only develop in “hard” materials. This is because an internal dipolar field requires the development of non-random, preferred defect distributions. This is only possible in modified PZT materials which contain significant concentrations of oxygen vacancies, such as that found in lower valent substituted (i.e., “hard”) PZT. Internal dipolar fields act conjugate to the order parameter P, similar to an externally applied positive DC bias. Both  $E_{int}$  and positive  $E_{dc}$  act as a force stabilizing particular domain configurations over others.

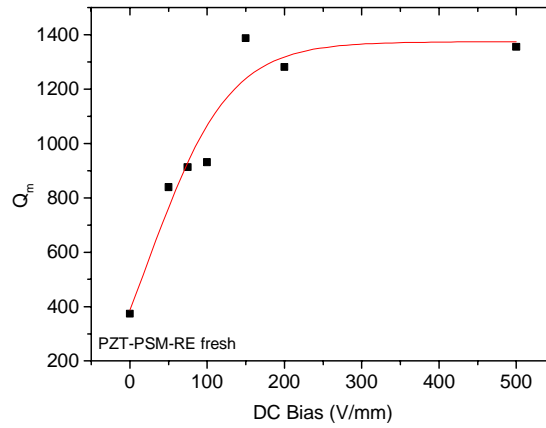


Figure 17  $Q_m$  value of “freshly” poled ferroelectrics as a function of applied DC bias for rare earth modified PZT-PSM

#### 4. Summary

In this paper the recent PZT-PSM based high power material development, loss mechanism analysis and possible high power origin investigation have been reviewed and discussed. Several of points can be summarized as following:

##### *PZT-PSM based high power materials development:*

1. Under high level drive conditions,  $v_o$  has been significantly increased by all of RE substitution investigated in this research, relative to that of the base PZT-PSM ceramic. PZT-PSM modified with 0.2 at.% Yb has been identified as a new high-power material. It has a  $v_o$  ( $T=20^\circ\text{C}$ ) as high as 0.9 m/s (rms value) under an electric field of 10 kV/m (rms value), which is about 2 times higher than that of the commercial “hard” ceramics where  $v_o$  ( $T=20^\circ\text{C}$ ) is equal to 0.4 m/s.
2. Most RE transition-metal substituents investigated in the study have been shown to result in combinative “hardening” and “softening” doping effects in PZT-PSM ceramics, regardless of the ionic radii. Both  $Q_m$  and  $k_{31}$  value was increased upon the RE substitution. No proportional relationship was found between the substituent RE ionic size and the electromechanical properties in this complex system, which is different from that of pure PZT. Mechanical quality factor  $Q_m$  has been significantly increased by doping with several RE species under both high and low level of drive.

##### *High power piezoelectric characteristic origin investigation*

3. The time dependences within 48 hrs after poling of electromechanical characterizations showed a significant increase of  $Q_m$  with time for “hard” PZTs, however no such change was observed for the “soft” ones. The aging rate after poling was found related to the degree of “hard” characteristics. The data indicate that “hard” piezoelectric behavior (i.e., an increase

of  $Q_m$ , decrease of  $k_{31}$ ,  $S_{11}^E$  and  $K$ ) is due to the development of an internal dipolar field with time, via oxygen vacancy diffusion towards an energetically favored site in lower valent modified PZT. Vibration characterization suggests the internal dipolar field is essential for high power piezoelectric performance.

4. Electromechanical characterization of “freshly” poled RE substituted PZT-PSM has been performed under various applied DC biases ( $E_{dc}$ ) and for various aged conditions. The comparison of internal dipolar field ( $E_{int}$ ) and positive DC bias ( $E_{dc}$ ) have shown that they are the same as both stabilize preferred domain structures, lowering the loss factors.

#### *Loss Mechanism Investigation*

5. It was proposed that the extensive dielectric loss increases significantly with the increasing of the applied electric field, while the extensive elastic loss is rather insensitive to the applied compressive stress. Considering that both intensive dielectric and mechanical losses are composed of extensive dielectric and mechanical, it seems under high level of excitation for both resonance and antiresonance modes heat generation mainly comes from the extensive dielectric loss (Uchino, 2001).
6. Under high drive conditions,  $E_{int}$  should play an important role in increasing  $Q_m$  and obtaining of higher vibrational velocities within a specific temperature range. Enhanced domain stability by  $E_{int}$  should be the most important factor for lowering the loss factors and raising  $Q_m$ . Materials with high  $E_{int}$  (i.e., reduced loss and higher  $Q_m$ ) but reduced pinning effects would be ideal. Rare earth modified PZTs have excellent combinatorial properties in these regards.

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